variational principle and Schrödinger equation

normalized wavefunctions

energy functional $E[\psi] = \langle\psi|H|\psi\rangle$

variation

$$\begin{aligned} E[\psi+\delta\psi] &= \langle\psi|H|\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle + \langle\delta\psi|H|\delta\psi\rangle \\ &= E[\psi] + \delta E[\psi] + \mathcal{O}^2(\delta\phi) \end{aligned}$$

functional derivative $\dfrac{\delta E[\psi]}{\delta\psi} = \dfrac{E[\psi+\delta\psi] - E[\psi]}{\delta\psi}$

ensure normalization via Lagrange multiplier

$$L[\psi] = E[\psi] - \varepsilon\left(\langle\psi|\psi\rangle - 1\right)$$

variational principle

$$0 = \delta L[\psi] = \langle\delta\psi|\Big(H|\psi\rangle - \varepsilon|\psi\rangle\Big) + \Big(\langle\psi|H - \varepsilon\langle\psi|\Big)|\delta\psi\rangle$$

gives time-independent Schrödinger equation

variational principle and finite basis set

trial function $|\psi\rangle = \sum_n \alpha_n |\psi_n\rangle$ (orthogonal basis)

$$E[\psi] = \sum_{n,m} \alpha_n \alpha_m \langle \psi_n | H | \psi_m \rangle$$

$$L[\psi] = \sum_{n,m} \alpha_n H_{nm} \alpha_m - \varepsilon \left(\sum \alpha_n^2 - 1 \right)$$

variational principle

$$0 = \frac{\partial L}{\partial \alpha_k} = \sum_n \alpha_n H_{nk} + \sum_m H_{km} \alpha_m - 2\varepsilon \alpha_k = \left(\sum_n \alpha_n H_{nk} - \varepsilon \alpha_k \right) + \left(\sum_m H_{km} \alpha_m - \varepsilon \alpha_k \right)$$

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix} = \varepsilon \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix}$$

non-orthogonal basis set

trial function $|\psi\rangle = \sum_n \alpha_n |\psi_n\rangle$ (arbitrary basis)

overlap matrix $S_{nm} = \langle\psi_n|\psi_m\rangle$

$$L[\psi] = \sum \alpha_n H_{nm} \alpha_m - \varepsilon \left(\sum \alpha_n S_{nm} \alpha_m - 1 \right)$$

variation results in generalized eigenvalue problem

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix} = \varepsilon \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix}$$

tight-binding

$$H = -\frac{1}{2}\Delta + \sum V_n$$

superposition of well separated potentials V_n

use solutions of individual potentials

$$H_n = -\frac{1}{2}\Delta + V_n \qquad H_n|n\rangle = \varepsilon_n|n\rangle$$

as basis set

tight-binding approximation for matrix elements:

$$\begin{aligned}
\langle n|H|n\rangle &= \varepsilon_n + \sum_{m\neq n} \langle n|V_m|n\rangle \\
\langle n|H|m\rangle &= (\varepsilon_n + \varepsilon_m)/2\ \langle n|m\rangle + \langle n|V_n + V_m|m\rangle/2 + \sum_{k\neq n,m} \langle n|V_k|m\rangle
\end{aligned}$$

for n and m nearest neighbors

Hellmann-Feynman theorem & forces

molecular dynamics:

$$H(R_\alpha)|\Psi(R_\alpha)\rangle = E(R_\alpha)|\Psi(R_\alpha)\rangle$$

force on nucleus α

$$\vec{F}_\alpha = -\vec{\nabla} E(R_\alpha) = -\langle\Psi(R_\alpha)|\vec{\nabla} H|\Psi(R_\alpha)\rangle$$

$$\begin{aligned}
\frac{\partial}{\partial R_\alpha} E(R_\alpha) &= \langle\frac{\partial\Psi}{\partial R_\alpha}|H|\Psi\rangle + \langle\Psi|\frac{\partial H}{\partial R_\alpha}|\Psi\rangle + \langle\Psi|H|\frac{\partial\Psi}{\partial R_\alpha}\rangle \\
&= \langle\Psi(R_\alpha)|\frac{\partial}{\partial R_\alpha} H(R_\alpha)|\Psi(R_\alpha)\rangle + E(R_\alpha)\ \underbrace{\frac{\partial}{\partial R_\alpha}\underbrace{\langle\Psi(R_\alpha)|\Psi(R_\alpha)\rangle}_{=1}}_{=0}
\end{aligned}$$

for non-degenerate state ...

Hellmann-Feynman theorem

degenerate perturbation theory in Phys. Rev. B 2003 !

PHYSICAL REVIEW B **68**, 033105 (2003)

Hellmann-Feynman theorem at degeneracies

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The Hellmann-Feynman theorem is extended to account for degenerate states. Given a point $\lambda=\lambda_0$ in parameter space where the energy $E(\lambda_0)$ is n-fold degenerate, it is shown that the corresponding n forces (slopes) are obtained by diagonalizing the derivative of the Hamiltonian, $-\partial H(\lambda)/\partial\lambda|_{\lambda=\lambda_0}$, in the subspace of degenerate eigenstates. Such a rotation within the subspace of degenerate eigenfunctions is easy and simple to apply in practical calculations and should be performed *separately* for each independent direction in parameter space for which the forces are to be calculated.

DOI: 10.1103/PhysRevB.68.033105 PACS number(s): 31.15.Md, 03.65.−w, 71.15.−m

Hellmann-Feynman theorem (HFT)[1,2] is widely used in practice to calculate forces (slopes) in atoms, molecules and crystals, but the way it appears in Refs. 1 and 2 and in quantum mechanics textbooks (see, e.g., Ref. 3) is only correct for nondegenerate states (see below). It should be mentioned that there exists a more general form of HFT, which is defined also for off-diagonal matrix elements (see, e.g., Refs. 4–9). However, the prescribed expressions do not provide an

depend also on the *direction* (in parameter space) for which one calculates the forces. Practically, a set of degenerate eigenfunctions obtained in a numerical calculation has to be appropriately rotated to allow for the correct calculation of forces as expectation values of $-\partial H(\lambda)/\partial\lambda$ [see Eq. (1)] at degeneracy. These detailed and relevant points, all related to the "freedom" to chose the linear combinations of eigenstates at degeneracy, have been overlooked previously.

Hellmann-Feynman theorem II

a surprising failure of reason...

PHYSICAL REVIEW B **66**, 033110 (2002)

Breakdown of the Hellmann-Feynman theorem: Degeneracy is the key

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The Hellmann-Feynman theorem is a powerful and popular method to efficiently calculate forces in a variety of dynamical processes, but its validity has rarely been addressed. Here a surprising failure of this theorem is reported. The forces calculated by the theorem can be more than fifty times smaller than the forces calculated by the finite differential method. Numerical evidence shows that the energy-level degeneracy is the main reason. An analytical proof reveals that although eigenvalues do not depend on a linear combination of degenerate wave functions, forces do sensitively depend on it, which leads to ill-defined forces. A scheme is proposed to overcome this difficulty.

DOI: 10.1103/PhysRevB.66.033110 PACS number(s): 71.15.−m

The Hellmann-Feynman theorem[1] is powerful and has been widely used in many fields such as dynamical processes,[2] molecular dynamics,[3] chemical reactions, and

merical examples for C_{60} explicitly show that forces calculated by the Hellmann-Feynman theorem can be fifty times smaller than forces calculated by the finite differential

Hellmann-Feynman theorem III

an elegant method...

PHYSICAL REVIEW B **69**, 167102 (2004)

Extended Hellmann-Feynman theorem for degenerate eigenstates

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In a previous paper, we reported a failure of the traditional Hellmann-Feynman theorem (HFT) for degenerate eigenstates. This has generated enormous interest among different groups. In four independent papers by Fernandez, by Balawender, Hola, and March, by Vatsya, and by Alon and Cederbaum, an elegant method to solve the problem was devised. The main idea is that one has to construct and diagonalize the force matrix for the degenerate case, and only the eigenforces are well defined. We believe this is an important extension to HFT. Using our previous example for an energy level of fivefold degeneracy, we find that those eigenforces correctly reflect the symmetry of the molecule.

DOI: 10.1103/PhysRevB.69.167102 PACS number(s): 71.15.−m

The Hellmann-Feynman theorem (HFT) (Ref. 1) is an efficient method, but when eigenstates are degenerate, an extension is necessary. The reason is that any good linear combinations among degenerate eigenstates are still good

culated from two different configurations of C_{60}, the pristine and excited C_{60}. The fivefold degenerate case is from the pristine C_{60}. We present the force matrix elements in Table I.

exam

written test

Thursday, 19 February 2015

09:30-12:00

GRS Lecture Hall, Jülich

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hand-written notes of your choice

remember to have your
Studentenausweis with you